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Magnetic Coupling in CuCr_2X_4 ($\text{X} = \text{S}, \text{Se}$) Spinel Compounds Obtained via Substitution of the Chromium Ions by Nonmagnetic Sb or Al Ions

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Taking into account both the dc magnetic susceptibility and the magnetization measurements as well as the high-temperature expansion of the magnetic susceptibility procedure the hopping integrals and superexchange integrals for the first and second coordination sphere were evaluated. The two hopping integrals are positive and many times greater than the superexchange ones. The obtained results testify to that in the stoichiometric compounds under study the double-exchange magnetic interaction is the main mechanism responsible for very strong, ferromagnetic coupling. Using the total hopping integral B the bandwidth of mixed valence band of chromium ions was determined.

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1. Introduction

As it was related in [1], on the base of the spinel matrices CuCr_2S_4 and CuCr_2Se_4 , four spinel families were obtained via substitution in the B -sites of the magnetic chromium ions by the nonmagnetic Sb or Al ions. Three of these families turned out to be stoichiometric: $\text{CuCr}_{2-x}\text{Sb}_x\text{S}_4$ ($x = 0.3, 0.4, 0.5$) [1], $\text{CuCr}_{2-x}\text{Sb}_x\text{Se}_4$ ($x = 0.1, 0.2, 0.5, 0.8, 1.0$) [2], $\text{CuCr}_{2-x}\text{Al}_x\text{Se}_4$ ($x = 0.1, 0.2, 0.3, 0.4, 0.5$) whereas the fourth one, namely: $\text{Cu}_{1+x}\text{Cr}_{1.5+y}\text{Sb}_{0.5+z}\text{Se}_{4+t}$ (where $-0.02 \leq x \leq 0.01$, $0.03 \leq y \leq 0.35$, $-0.2 \leq z \leq -0.02$, $0.01 \leq t \leq 0.08$) [3] occurred to be nonstoichiometric. From the extended magnetic measurements of both the magnetization and the magnetic susceptibility it follows that:

- i) the spin glass states appear in all the compounds in which magnetic chromium sublattice is diluted by nonmagnetic antimony ions [2–4],
- ii) both the stoichiometric compounds with sulfur anion and the nonstoichiometric ones with the selenium anion magnetize very hard. In spite of the external magnetic field applied up to 14 T the samples belonging to these two spinel families are still far from magnetic saturation,
- iii) the lack of the magnetic saturation as well as the change of the slope of the rectilinear segments in the magnetization isotherms testify to that in all these samples magnetic spin-flop phase transitions take place,
- iv) in the stoichiometric antimony compounds with the

selenium anions, only the sample containing the antimony concentration x equal to 0.1 reaches the magnetic saturation,

- v) with the increase of the Sb concentration x in these compounds the magnetization decreases very fast and the magnetization processes become more and more hard. Moreover, the magnetization isotherms exhibit the hysteresis phenomena and very large paraproceses [3],
- vi) all the samples containing Al magnetize very easily and reach the magnetization saturation at very low magnetic field.

The aim of this paper is to discuss the mechanisms which are responsible for magnetic coupling in the compounds under study as well as to determine the contributions to the whole exchange energy coming from these mechanisms.

2. Experimental

For the compounds under study both the dc and ac magnetic susceptibility were measured. The dc measurements were carried out with the aid of the Cahn magnetic balance whereas the ac measurements were carried out with the use of the Lake Shore magnetometer. The examples of the dc magnetic susceptibility obtained for stoichiometric compounds are presented in Figs. 1 and 2, whereas the most important magnetic parameters for these compounds are presented in Table I.

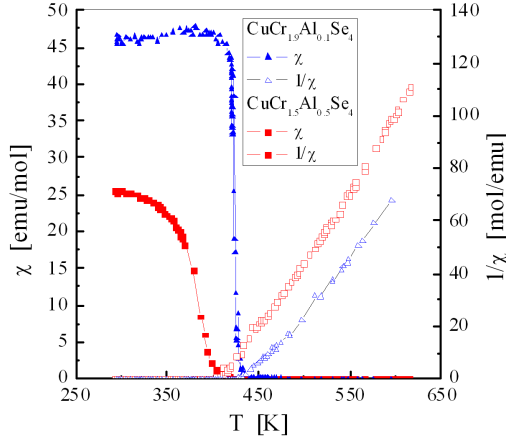


Fig. 1. The magnetic susceptibility and its reciprocal as a function of temperature for $\text{CuCr}_{1.9}\text{Al}_{0.1}\text{Se}_4$ (tri-angle) and $\text{CuCr}_{1.5}\text{Al}_{0.5}\text{Se}_4$ (square).

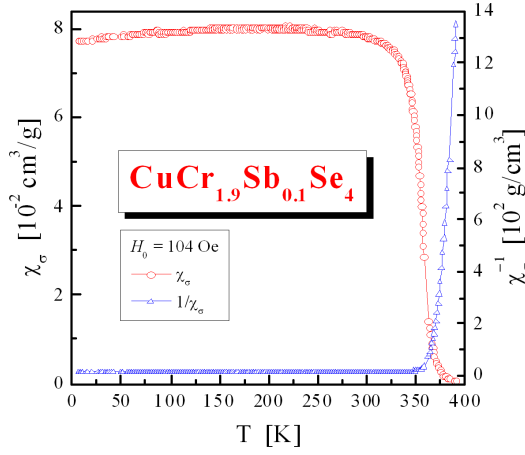


Fig. 2. The magnetic susceptibility and its reciprocal as a function of temperature for $\text{CuCr}_{1.9}\text{Sb}_{0.1}\text{Se}_4$ [3].

TABLE I

The most important magnetic parameters of the spinels under study.

| Compound | μ_s [μ_B] | μ_{ef} [μ_B] | T_c [K] | Θ_{c-w} [K] |
|---|------------------------|---------------------------|--------------|-----------------------|
| CuCr_2Se_4 [5] | 4.76 | 5.21 | 416 | 436 |
| $\text{CuCr}_{1.9}\text{Al}_{0.1}\text{Se}_4$ | 5.98 | 4.09 | 428 | 454 |
| $\text{CuCr}_{1.8}\text{Al}_{0.2}\text{Se}_4$ | 5.35 | 4.50 | 435 | 446 |
| $\text{CuCr}_{1.7}\text{Al}_{0.3}\text{Se}_4$ | 5.28 | 4.00 | 411 | 439 |
| $\text{CuCr}_{1.6}\text{Al}_{0.4}\text{Se}_4$ | 5.19 | 3.93 | 402 | 427 |
| $\text{CuCr}_{1.5}\text{Al}_{0.5}\text{Se}_4$ | 4.61 | 3.75 | 399 | 423 |
| $\text{CuCr}_{1.9}\text{Sb}_{0.1}\text{Se}_4$ | 5.71 | 5.47 | 357 | 375 |

3. Results and discussion

In the compounds under study exchange couplings between magnetic moments localized on the chromium ions can be realized via three following types of magnetic interactions: (i) the superexchange with the interactions paths: $\text{Cr}^{3+}-\text{X}^{2-}-\text{Cr}^{3+}$, $\text{Cr}^{3+}-\text{X}^{2-}-\text{X}^{2-}-\text{Cr}^{3+}$, $\text{Cr}^{3+}-\text{X}^{2-}-\text{A}^{2+}-\text{X}^{2-}-\text{Cr}^{3+}$, (ii) the Zener double-exchange between $\text{Cr}^{3+}-\text{Cr}^{4+}$ ion pairs, (iii) Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction caused by the appearance in the matrices of the itinerant electrons coming from the existence in them of a few percent of the Cu^{2+} ions [3]. Because the crystal field of the ligands splits every 3d level of the cations into the triplet t_{2g} and the doublet e_g the different overlaps (so called: σ , π and Δ) are possible of the wave functions 3d with the p orbitals of anions. The octahedral coordination of Cr^{3+} ions causes that their e_g orbitals participating in the coupling via σ -band are empty whereas their t_{2g} orbitals participating in the coupling via π -band are half-filled. According to the Goodenough–Kanamori rules the couplings of the type $\sigma-\Delta-\sigma$ and $\pi-\Delta-\pi$ are antiferromagnetic, whereas $\sigma-\Delta-\pi$ coupling is ferromagnetic. As concerns the double-exchange mechanism of interactions, it gives both ferromagnetic and very strong coupling of magnetic moments.

From the magnetic susceptibility measurements it follows that for the compounds under study with micro-magnetic ordering the superexchange interaction appearing simultaneously with the double-exchange interactions dominates. On the other hand, in the compounds containing Al, double-exchange interaction absolutely dominates, giving very high values of both Curie (T_c) and Curie–Weiss (θ_{CW}) temperatures. This qualitative analysis, which was made on the base of the results contained in [1] as well as in this paper indicates that in the compound under study apart from the exchange interaction the double-exchange interaction appears. So double-exchange interaction becomes responsible for the very strong magnetic coupling of the magnetic moments in these compounds. The quantitative contribution of the double-exchange in the total exchange integral was calculated on the ground of the high temperature expansion of the magnetic susceptibility [5].

The results of the utilization of this method are the equations describing the contributions to the paramagnetic Curie–Weiss temperature coming from the separate mechanisms of the exchange interactions. Because in the spinels under study the essential role is played by both the superexchange and the double-exchange interactions, the equation for the paramagnetic Curie–Weiss temperature has the following form:

$$\Theta_{c-w} = \Theta_{sex} + \Theta_{dex}, \quad (1)$$

where Θ_{c-w} is the paramagnetic Curie–Weiss temperature (from experiment), Θ_{sex} is the contribution to the Θ_{c-w} coming from superexchange, Θ_{dex} is the contribution to the Θ_{c-w} coming from double-exchange. Moreover,

$$\Theta_{\text{sex}} = (2/3)X\Theta, \quad (2)$$

where $\Theta \approx 150$ K denotes here an average value of the paramagnetic Curie–Weiss temperature coming from the superexchange interaction in the spinel compounds and

$$X = x_3(3/2)(3/2 + 1) + x_4 1(1 + 1), \quad (3)$$

where x_3 is the concentration of Cr^{3+} ions with the spin $S = 3/2$, x_4 is the concentration of Cr^{4+} ions with the spin $S = 1$. Concentrations x_3 and x_4 were calculated from the saturation magnetization M :

$$M = 2(g_4 x_4 + g_3 x_3 3/2), \quad (4)$$

taking into account that in the matrixes CuCr_2S_4 and CuCr_2Se_4 one half of the chromium ions is Cr^{3+} and another one is Cr^{4+} , the values of the Landé factors are $g_4 = 1.86$ and $g_3 = 2$, respectively. The following normalization condition is valid:

$$x_3 + x_4 = 1, \quad (5)$$

where B stands for the total hopping integral for the first and second coordination spheres. Substituting (2), (3) and (5) into (1) one obtains an equation with B being unknown

$$\Theta_{\text{c-w}} = (2/3)X\Theta + (1/6)Xx_3(1 - x_3)B. \quad (6)$$

The total hopping integral B calculated from Eq. (6) can be written down as follows:

$$B = 6b_{aa} + 36b_{ab}, \quad (7)$$

where b_{aa} stands for the contribution from the 6 nearest neighbors (with the distance to a given ion equal to $0.354a$) and b_{ab} stands for the contribution from the 36 second nearest neighbors (with the distance to a given ion equal to $0.704a$); a is the lattice parameter. On the ground of the Lotgering considerations [6] one can find that the ratio b_{aa}/b_{ab} is equal to 5. This made it possible to calculate the values of hopping integrals per pair of ions Cr^{3+} – Cr^{4+} for the first and second coordination spheres. Using Eq. (2) and the results of Ref. [7] the superexchange integrals J_{aa} and J_{ab} between the two ions from the first and second coordination spheres have been calculated. The obtained results are presented in Table II.

As it follows from Table II the exchange integrals connected with the double-exchange are positive for the two coordination spheres. One can easily see that all these integrals are many times greater than J_{aa} . Thus, this quantitative analysis has proved that in stoichiometric compounds under study the double-exchange interaction is the main mechanism responsible for the strong, ferromagnetic coupling. Moreover, taking into account the total hopping integral B listed in Table II we can get the bandwidth of the $3d$ t_{2g} band connected with the mixed

valence of Cr^{3+} – Cr^{4+} . For the compounds containing Al the bandwidth of the $3d$ t_{2g} band due to Cr ions is then $W_d = 2B = 5400 \pm 500$ K $\cong 0.49 \pm 0.05$ eV. On the other hand, for the compound containing Sb such bandwidth is $W_d = 2B = 3520 \pm 100 = 0.32 \pm 0.01$ eV. For comparison the chromium mixed valence bandwidth W_d in the CuCr_2Se_4 matrix is equal to 0.63 ± 0.05 eV [5]. It is worthy to underline that this fundamental parameter of electronic structure has been found from an interpretation scheme of our magnetic measurements.

TABLE II

The exchange integrals following from both the double exchange and superexchange magnetic interactions for the compounds under study.

| Compound | B [K] | b_{aa} [K] | b_{ab} [K] | J_{aa} [K] | J_{ab} [K] |
|---|------------|-----------------|-----------------|-----------------|-----------------|
| CuCr_2Se_4 [5] | 4391 | 969.3 | 27.3 | 16.9 | −8.50 |
| $\text{CuCr}_{1.9}\text{Al}_{0.1}\text{Se}_4$ | 3218 | 243.8 | 48.8 | 17.2 | −1.43 |
| $\text{CuCr}_{1.8}\text{Al}_{0.2}\text{Se}_4$ | 2601 | 197.0 | 39.4 | 16.1 | −1.45 |
| $\text{CuCr}_{1.7}\text{Al}_{0.3}\text{Se}_4$ | 2631 | 199.3 | 39.9 | 17.1 | −0.44 |
| $\text{CuCr}_{1.6}\text{Al}_{0.4}\text{Se}_4$ | 2667 | 202.0 | 40.0 | 16.5 | −0.32 |
| $\text{CuCr}_{1.5}\text{Al}_{0.5}\text{Se}_4$ | 2401 | 181.9 | 36.4 | 15.5 | −0.21 |
| $\text{CuCr}_{1.9}\text{Sb}_{0.1}\text{Se}_4$ | 1764 | 133.7 | 26.7 | 18.8 | −0.60 |

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